Experimental Electron Density Study of an Organozirconium Compound

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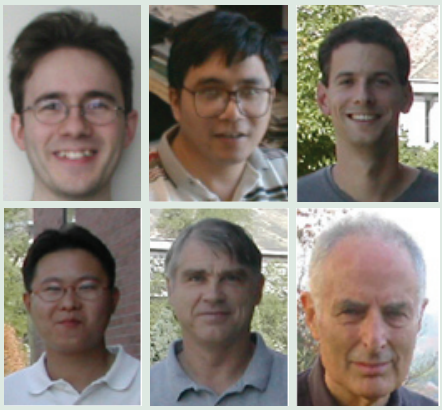
Scientists at the State University of New York in Buffalo and at the University of Utah have synthesized a novel organozirconium complex and subjected it to a careful experimental electron density study at 16 K. The study demonstrates that it is now possible to achieve accurate results for such heavier atom-containing species when high intensity sources and small crystal sizes are employed. The analysis of the electron density distribution for the organozirconium complex has revealed unusual 4d orbital populations and provided insight both into the nature of the bonding of the zirconium center to its various ligands, and into a number of interatomic contacts between formally nonbonded atoms.

In electron deficient organometallic compounds, it is not uncommon for empty orbitals on a metal center to interact with electron pairs in nearby C-H bonds. That was certainly what was expected to be found in **Complex 1**, in which a very small Zr-N-C angle indicated there was some sort of interaction between Zr and the isopropyl group. However, spectroscopic data did not give any indication of such an interaction. This led the researchers to undertake an experimental electron density study of the compound, even though a truly accurate study of a compound with an atom as heavy as zirconium had never been achieved before. The high intensity X-rays provided by the NSLS and high-resolution single-crystal facilities at the SUNY X3 beamline were indispensable in this undertaking.

Despite the inherent obstacles to overcome in obtaining accurate data, the researchers were rewarded with a variety of interesting results, although ironically they ultimately did not find an unambiguous answer to the question that had prompted the study, which concerned the putative agostic interaction between the metal center and a proximal C,H region. To begin with, the d orbitals on zirconium were found to exhibit unusual populations based on ligand field considerations. Three orbitals (d_{z^2}, $d_{x^2-y^2}$, and d_{xz}) were found to be relatively highly populated, indicating σ donor interactions from the organic ligands, and both σ and π donor interactions from the nitrogen center, respectively.

The study also revealed significant details concerning the bonding electrons in the compound. A topological analysis of these electrons showed "bond paths" for all the expected bonds between the lighter atoms. However, bond paths were only found between the zirconium atom and three ligand atoms (N and two C). Many of the carbon atoms to which Zr is presumably bonded were not found to be connected to the Zr atom by bond paths. Thus, not only were there no bond paths connecting the Zr with the isopropyl group, but there were also no bond paths to four of the five dienyl carbon atoms (**Figure 1**), and three of the four diene carbon atoms. Nonetheless, the electron density distributions and ellipticities, together with the actual placement of the zirconium atom, provided clear evidence for the presence of interactions between these ligand atoms and the zirconium center. As topological analyses have



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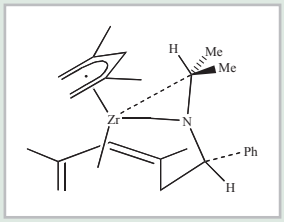
only recently begun to be employed to characterize the bonding in types of organometallic compounds, this result provides guidance for further studies using this method.

An unexpected bonus was provided by the observation that the p-orbital electron densities of the diene and dienyl π systems were not oriented perpendicular to their atomic planes, but rather experienced "tilts" or rehybridizations in order to be directed more toward the zirconium center. Such tilts had previously been inferred from distortions exhibited by π ligand substituents, but this is the first direct experimental evidence for these reorientations. As noted above, the charge density analysis did not provide direct evidence for the existence of an agostic interaction (**Figure 2**).



Complex 1

The topological analyses also revealed interesting interactions between some formally nonbonded atoms. Intermolecular CH/π and π/π interactions were observed between dienyl ligands in adjacent complexes, while a more unusual bond path was observed between opposing hydrogen atoms present on the dienyl ligand termini. This interaction may account for the observed tendency of pentadienyl ligands under some conditions to undergo loss of H_2, yielding the more common cyclopentadienyl ligand.

While this study has yielded substantial insight into the bonding of this compound, very few electron density studies have been carried out on organometallic compounds in general. One can therefore expect that a wealth of additional new information will be achieved through similar studies of a wide variety of organometallics.

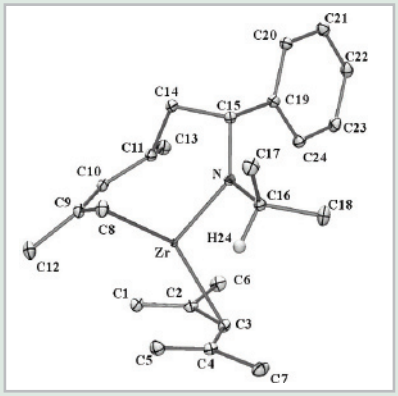


Figure 1. Illustration of the experimentally determined bond paths in the organozirconium complex.

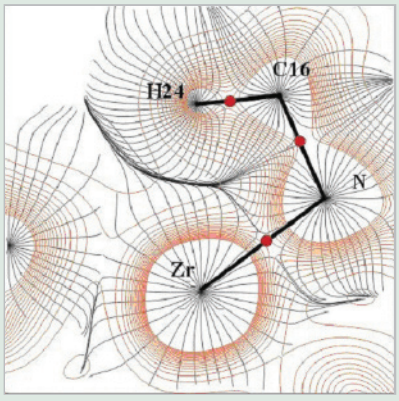


Figure 2. Electron density gradient trajectories (grey lines) and total electron density (red lines) for the Zr-N-C-H plane. Bond critical points are depicted as red circles. Contour levels of 0.1 eÅ^{-3} are used for the electron density.